6.0 INTERPRETATION OF ANALYTICAL DATA

The first step in the interpretation of analytical data is the review of data submitted by laboratories, responsible parties and/or project managers. During this process, the evaluator initially establishes the data validation validity.

Analytical data that exceed regulatory criteria often reflect violations of waste regulations and trigger remediation. At times, the process of remediation may involve litigation. So, analytical data can be an important component of evidence and as such should be legally defensible. It is then essential that evaluators establish validity of data to be presented as reliable evidence.

Data validation should take into account both sampling and analysis because both may contribute to errors in the results. It is important to locate sources of error arising from sampling and analysis. Merely evaluating the laboratory analysis is not a substitute for evaluating the entire process. Sampling in the field and subsequent sub-sampling in the laboratory are typically the areas where the process is the least certain. It is therefore particularly important that these steps be included when evaluating data.

6.1 GENERAL REQUIREMENTS.

Generally, Sampling and Analysis Plans (SAPs), Waste Analysis Plans (WAPs) and Quality Assurance Project Plans (QAPPs) require prior approval by EPA or Cal-EPA. Data that have been generated without the use of approved plans may have deficiencies and may be unusable for the intended purpose. On request, personnel at ECL evaluate such plans for compliance and completeness.

Field sampling procedures, laboratory analytical methods and quality assurance protocols must be clearly stated in the above documents. Laboratories performing the specified analyses must be certified/accredited by the Environmental Laboratory Accreditation Program (ELAP).

6.2 INDICATORS OF DATA QUALITY.

The typical indicators of data quality are precision which measures random error, accuracy which measures systematic error, comparability, representativeness, completeness and existence or non-existence of sample contamination. Other factors to consider are detection limits, blunders, and fraud.

6.2.1 Precision:

Precision is measurement of random error. It is the degree of agreement between two or more measurements. The simplest way to report precision is as Relative Percent

Difference (RPD). RPD is calculated as the difference between two measurements divided by their mean. The Range (R), Standard Deviation (s), and Coefficient of Variation (CV) or Relative Standard Deviation (RSD), are also used as measures of precision. A small RSD or RPD indicates high precision. RSD and RPD are fractions of the measurement which can be converted to limits about the mean. For example: 50 mg/kg ±5 mg/kg or 50 mg/kg ±10%.

Precision as relative percent difference (RPD) is calculated as:

$$RPD = \frac{|X_1 - X_2|}{\bar{x}} \times 100$$

where X_1 and X_2 are duplicate analyses and $\bar{x}$ is the mean value of the two values.

$$\%RSD = \frac{s}{\bar{x}} \times 100$$

The relative standard deviation or coefficient of variation:

where *s* is the sample standard deviation.

$$RPD = \%RSD \times \sqrt{2}$$

The relationship between the *RPD* and the *% RSD* is:

Precision for the entire measurement process is best determined using homogeneous split samples. Laboratory replicates (typically duplicates) indicate intralaboratory (within laboratory) precision for the analysis. Laboratories sometimes run duplicates through only a portion of the analysis. It is important to distinguish between those duplicates that represent the entire analysis and those that may, for example, only represent the instrumental step and exclude the sample preparation part.

Sometimes matrix spike and matrix spike duplicates (MS/MSDs) are used instead of duplicates to measure precision. When duplicates do not have any analytes, analyses of duplicates do not provide any data on precision. Analysis of MS/MSD assures the

availability of precision data.

MS and MSDs are analyzed once for every batch of samples or every matrix or every twenty samples whichever is more frequent.

Precision is determined by duplicate or MS/MSD analyses. Precision should be monitored and documented for each parameter and matrix routinely run in the laboratory. At a minimum, water and soil results should be monitored. When the control limits for precision are exceeded, corrective action should be initiated or an explanation should be included in the laboratory report.

6.2.2 Accuracy:

Accuracy (or freedom from bias) is the agreement with the true value. Accuracy is usually determined by spiking samples with a known amount of analyte. The ratio of the measured amount to known amount is termed the recovery, which is expressed as a percentage. Spiked sample accuracy as percent recovery (R) is calculated as:

$$R = \frac{(C - X)}{T} \times 100$$

where C is the measured spike sample value
X is the unspiked sample value
T is the value of spike added

The spikes are usually added to the sample before it is extracted or digested and carried through the entire preparative and analytical scheme. Such spikes are called laboratory matrix spikes. When evaluating laboratory matrix spikes, it is important to determine the point in the procedure at which the sample was spiked. A sample that was spiked before preparation is used to determine percent recovery for the entire procedure. A spike introduced later in the analysis can be used for other reasons but cannot be used to determine percent recovery for the sample preparation or extraction.

Method spikes (method blanks spiked with reference standards) are used to demonstrate that the analytical system is operating within control limits and also at times to document unusual recoveries due to matrix effects.

In addition to matrix spikes, reference materials (i.e. materials certified by NIST which contain analytes of interest at known values) can also be used to assess accuracy. Such reference materials are usually used to validate methods, evaluate laboratories and/or analysts. They may also be used as external quality control samples.

When multiple analyses of a reference sample or multiple spikes of a matrix are run, the

standard deviation of the recoveries can be calculated. While it is not common that a project would require this level of QC, it is then possible to calculate the expected accuracy with a certain confidence. Refer to Reference 1 for an example and more information.

MSs are analyzed once for every batch of samples or every matrix or every twenty samples whichever is more frequent.

Accuracy is determined by external and/or internal check samples and matrix spikes. Accuracy is monitored and documented for each parameter and matrix routinely run in the laboratory. At a minimum, water and soil matrices are monitored. When the control limits for accuracy is exceeded, corrective action must be initiated before the analysis is completed.

6.2.3 Blank analysis to measure contamination:

Assessment of blank data is an important part of data validation. Several types of blanks are used.

Field blanks are valuable because they incorporate the entire measurement process. They are prepared in the field by the sample collector. When properly designed, they are submitted blind and analyzed and reported like any other sample. Contamination may occur in the field at the time of sampling through the use of contaminated equipment. Equipment blanks are used to measure such contamination. Travel blanks are used to monitor contamination that may occur during transportation. Finally laboratory contamination is monitored by the use of method blanks. Organic solvents used in sample extraction or equipment cleaning are typical contaminants. Methylene chloride and acetone commonly appear in volatile organics results (Method 8260). Phthalates, such as bis (ethylhexyl) phthalate and di (n-octyl) phthalate, are used as plasticizers and are frequently found in semivolatile organics (Method 8270) results.

When comparing blank and sample data, consideration must be given to the dilutions used in the analysis. If a high level sample needs to be diluted for analysis, that dilution must also be made to the laboratory blank. The concentration of a parameter in the blank would then be multiplied by the dilution factor. This can be a problem in volatile organic analyses because trace level contamination in the diluent water can be interpreted as a large amount of analyte in the original sample.

Field blanks, equipment blanks, trip blanks, etc. will be analyzed in addition as submitted. Method blanks shall be preformed at one per batch of samples per matrix type per sample extraction or preparation method.

Calibration blanks which are used to set the instrument as zero response are analyzed as specified by the manufacturer and/or protocol to demonstrate that the instruments are

properly calibrated.

Method blanks are checked for any contamination problems. Routinely, they contain no analytes. A possible exception to this rule is when common laboratory solvents such as Acetone, Methylene Chloride are detected in volatile analyses. Reports may be released for a particular study pending the correction of this problem if the results of the analyses are not compromised by this contamination problem.

Although analytical data are not usually corrected for contamination in sample blanks, it should be so noted. The concentration of any analytes found in the blanks will be reported as found. Routinely blank concentrations are not subtracted from the sample concentrations. It is advised that if blank concentrations need to be subtracted from sample concentrations control charts be maintained so that the long term contamination of a laboratory is definitively established and an averaged value is subtracted. Generally, analyte concentration in blanks are of concern when they are greater than 10% of the sample concentration or the method detection limit.

6.2.4 References

1. USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review, USEPA Office of Solid Waste and Emergency Response, OLMO 4.2 May 1999

2. USEPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review,USEPA Office of Solid Waste and Emergency Response, ILMO 5.3 March 2004

6.3 Method Detection Limits and Quantitation Limits:

There are several conventions for reporting results near the reporting limit. When in doubt about the meaning of a result, the reporting lab should be contacted. Statistical analysis of results below the reporting limit can be done by 1) substituting a value for the non-detect result, 2) assuming a distribution from the results above the reporting limit, or 3) "robust" statistical techniques. These techniques are reviewed and discussed in Helsel, 1990 (see references).

6.3.1 Method Detection Limit (MDL)

For all methods used at ECL and ECL-SC, except trace analysis, MDL is based on the statistical calculations of replicate sample matrix spikes as defined in "Appendix B to Part 136 - Definition and Procedure for the Determination of the Method Detection Limit - Revision 1.11," CFR, 49, No. 209, Friday, 10/26/84, 198-199). Specifically, the MDL is defined as

$$\mathbf{MDL = t_{(n-1,1-\alpha=0.99)} \times s}$$

where:

$t_{(n-1,1-\alpha=0.99)}$ = the student's t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom.

s = the standard deviation of the replicates analyses.

For the Dioxin and Furan analysis, the MDL is defined as

$$\mathbf{MDL = 3 \times s \times F}$$

where:

s = the standard deviation of the background noise level of the actual sample extract.

F = the sample extract dilution factor times any additional factors to account for matrix interferences.

MDL is three times the noise (background) of the sample.

In both cases, the MDL is calculated for the original sample matrix and not its resultant extract or digestate, i.e., dilution factors are applied to correct extract or digestate concentration back to the original sample concentration. MDLs will be applied primarily to laboratory reagent water and clean soil and generally not to the more complicated matrices,

such as sludges, as these matrices are more difficult to define.

6.3.2 Quantitation Limit (QL)

For the Organic, GC/MS and Inorganic Units, the QL is defined as

QL = LS x F

where:

LS = the lowest acceptable calibration standard (acceptable as defined for a linear response or by actual curve fitting).

F = the sample extract dilution factor times any additional factors to account for matrix interferences.

For the Dioxin and Furan analysis, the QL is defined as

QL = 10 x s x F

where:

s = the standard deviation of the background noise level of the actual sample extract.

F = the sample extract dilution factor times any additional factors to account for matrix interferences.

6.4 Reporting Criteria

6.4.1 Tentative Identification of Non-target Sample Compounds by GC/MS analysis

For samples containing compounds not associated with the calibration standards, a computer library search may be made for the purpose of tentative identification. The reference library used for the search is the NIST/EPA MSDS mass spectral library. The necessity to perform tentative identification will be determined by the analysis objective. The identification of the compound is dependent on the chromatographic resolution and spectral quality of the unknown compound. Guidelines presented in the method are used to making tentative identifications. An estimate of the concentration for non-target compounds of the sample will be based on the total ion chromatogram (TIC) areas of the closest internal standard and non-target compound as described in the method.

6.4.2 Terms and symbols used in the Dioxin and Furan Reports

* This symbol indicates that an analyte is below the MDL (minimum detectable level). In the case where a real dioxin was detected and quantified in a sample the MDL for that isomer in the sample is based on three times the noise (background) of the average blank. The MDL for that analyte is reported.

B This symbol indicates that an analyte was detected above the MDL but below the QL. The measured value is reported.

When an analyte is above the QL, that value is reported without any accompanying symbol.

In the case where analyte is detected in both the blank and the sample:

L This symbol indicates that analyte detected in the sample is also detected in the blank. The amount in the sample is less than three times the amount in the blank. The value reported is the upper limit of the concentration that could be in the sample. The blank is not subtracted.

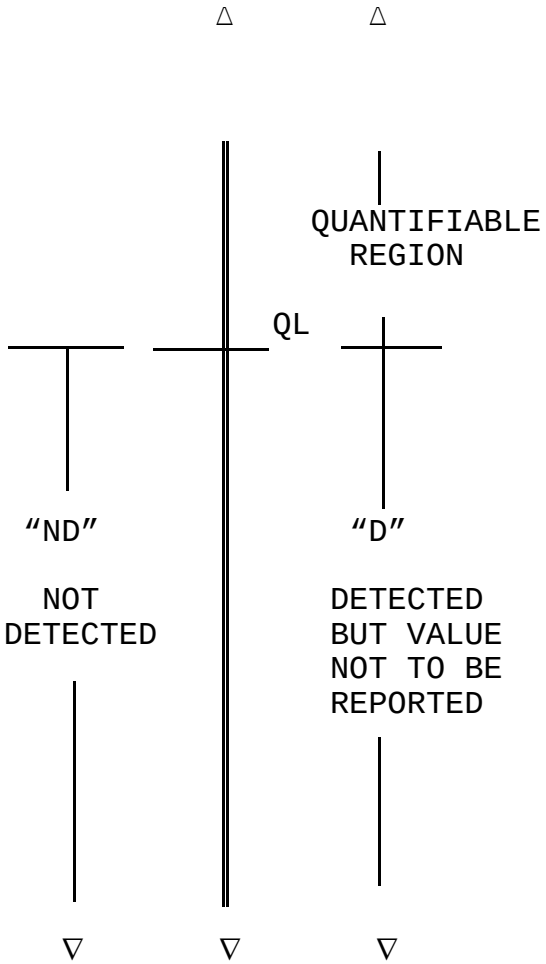
\# This symbol indicates that the analyte was detected in the blank and the sample. The amount in the sample is between three and ten times the amount detected in the blank. The value reported is the upper limit of the concentration that could be in the sample.

I This symbol indicates that the analytes was detected but interferences are present in the quantitation ion or the confirmation ion. The value reflects the upper limit of the concentration that could be in the sample.

6.4.1 Based on the previously defined limits (MDL and QL), the following diagrams describe the criteria used in ECL in the reporting of routine analytical results.
MDL not yet established (not applicable to EPA 6010 results).
Report analytical results ≥ QL.

Report detected results < QL as "D" (meaning "detected, but not quantitated, i.e. < QL), instead of the numerical results.

Report not detected results as "ND".



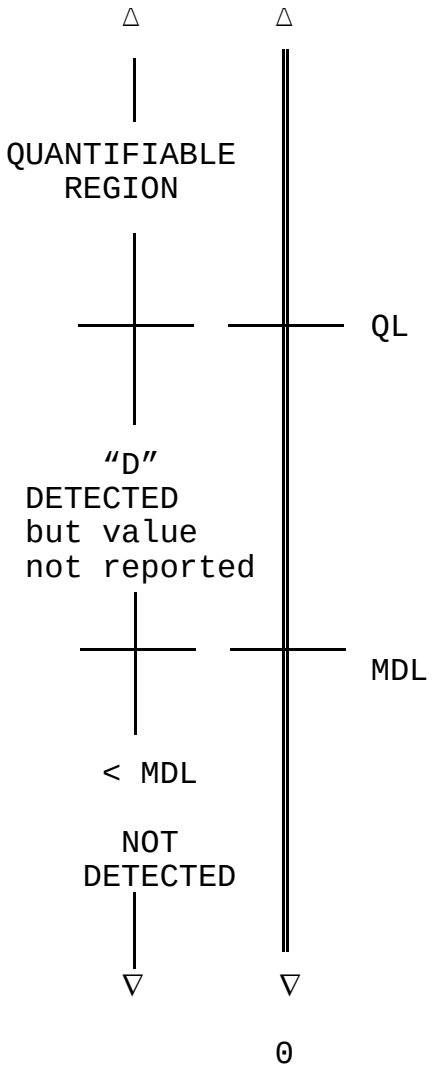
ANALYTE NOT DETECTED **ANALYTE DETECTED**

6.4.2 MDL established (not applicable to EPA 6010 results).

Report analytical results ≥ QL.

* Report results ≥ MDL but < QL, as "D" (meaning "Detected", but not quantitated I. e. < QL), instead of the numerical results.

Report results < MDL as "ND" (not detected).

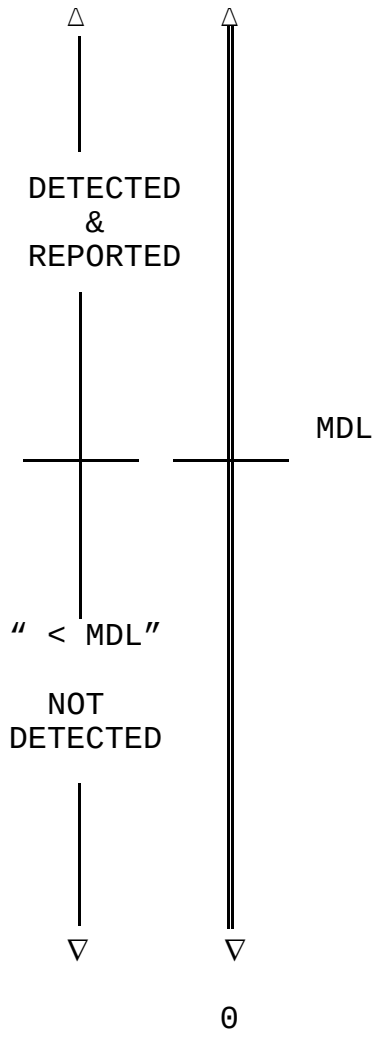


* Please note:
If requested for nonroutine analysis, estimated numerical values can be reported for results ≥ MDL but < QL

6.4.3 Reporting criteria for Method 6010 results.

Report analytical results ≥ MDL.

Report results < MDL as "< MDL value" for the respective elements.



6.5 Comparability:

In data assessment, the term comparability is used in different ways depending on the context.

It is not unusual for data from different laboratories to seemingly conflict. Typically the largest area of uncertainty is the sample itself. It is important to determine if the samples received by each laboratory were actually similar. Were the samples actual split samples? Were they shipped and preserved in the same way? Were they subsampled in the laboratory the same way? Were the samples homogenized during initial sample preparation? If the samples were not the same or if the samples were treated differently it is not reasonable to expect analytical results to agree.

Method comparison - In many cases the same method may be cited by both laboratories (e.g. EPA method 601) but the actual procedures performed may be substantially different. It is important to determine if the procedures used are appropriate to the analysis. Further, for example, if one data set were generated after an initial filtration step, the other data also should have been generated after a filtration step. If this fact cannot be documented the comparability of the data sets is in doubt.

Another common technique is the comparison of results for samples split between two or more laboratories.

Quality Control Data - Quality control sample data should be examined for all the data quality indicators given in sections 6.2. Detection limits should be compared. One laboratory may report a compound at a level of 4 mg/kg and while another laboratory reports Not Detected (ND). This is not a conflict if the limit of detection adopted by the latter laboratory is greater than 4 mg/kg. Another important consideration is blank analysis. Method blanks should be examined any time that one laboratory reports positive results and another ND, as the positive results may actually be laboratory contamination.

Ideally, interlaboratory comparisons of data should be performed only on data generated concurrently by the analysis of split samples.

One rule of thumb for labs using similar methods on homogeneous samples, is that results should agree within a factor of two (2). For example, if one lab reports 50 ppm, the other lab's results should be within 25 to 100 ppm. These limits are used by the EPA Office of Solid Waste when evaluating interlaboratory method performance data to accepted values. Where differences between labs cannot be resolved, the labs may exchange sample extracts, analyze performance evaluation samples, or re-analyze samples which are at issue. ECL can arrange these tasks for Cal-EPA staff.

6.6 Representativeness:

Representativeness refers to the extent to which the analytical results reported represents the site actually sampled. There are two areas in the sampling and analytical process that affect representativeness.

Sampling at the site by the sample collector is a crucial step in the entire sampling process in that the sample(s) collected should be representative of the material that is being sampled. If a bias is built into the sampling process, the representativeness of the sampling will be in question. Statistically valid random sampling processes should be used when sampling. If a biased sampling procedure is adopted for a particular site, adequate reasons for use of such a sampling scheme should be provided. All aspects of sampling should be well documented. Section 3 addresses these concerns in sufficient detail.

Samples brought into the laboratory are sub-sampled by the analyst to carry out a particular analytical method. This is referred to as representativeness at sub-sampling. Adequate controls must be established to assure that there is no bias introduced at subsampling. If the entire sample brought into the laboratory is homogenized and subsampled thereafter, variability due to subsampling is negligible.

6.7 Completeness:

The traditional definition of Completeness is an attempt to establish the degree of completion of the work specified in a project plan. The criterion for completion is typically set at 90%.

For example, if 5 surface samples, 10 subsurface samples and 5 well samples were collected and if each of these samples were to be analyzed for metals, VOAs, and semi-volatile organics; a project report would contain at least 90 % of the data specified. That is, a total of 20 samples with each sample analyzed by three methods, or 60 test results, should be reported. Further, each of these tests would have several analytes. Additionally, QC data specified in a QAPP would also be included in a typical report.

A more challenging aspect of completeness is to account for complete mass balance. That is, one would try to correlate the indicator parameters such as specific conductivity, total organic carbon, total organic halides, etc. to all tested analyte concentrations. If a discrepancy exists, this will give a measure of incompleteness. This approach is taken in certain specific circumstances when accounting for total mass is critical in the assessment of data quality.

6.8 Method References:

Field and analytical methods used should always be considered when evaluating data. Most methods will have QC requirements built into the procedures. Any additional QC procedures and their acceptance limits should be specified in the project plans.

Laboratory reports should include method references, sample matrix, method detection limits (MDL)/quantitation limits (QL) and reporting units. It is important that the methods used are those specified in the quality assurance project plans and are appropriate for the objectives of the study. A comparison should be made of the QC requirements in the stated method and those reported. If fewer QC samples were run than required or if QC samples reported are not within limits, then the results may not be valid. Obviously, sample data reported without method reference or QC data are highly uncertain and may not be usable for all purposes.

6.9 COMPARISON WITH REGULATORY LIMITS.

When analytical results are compared with regulatory limits, consideration must be made to recovery and precision data. In some cases, if a compound is reported as 4800 mg/L ± 10% and the regulatory limit is 5000 mg/L, then the result may be considered to be greater than the regulatory limit. This is because the confidence interval is 4320 to 5280 mg/L and the upper limit is greater than 5000. SW-846 uses the 80% confidence interval (two tailed) to determine whether a waste is hazardous. Where no uncertainty data are available and results are reported close to regulatory limits (i.e. within a factor of two), the reviewer should rely on precision data and experience with data from similar situations to determine if more analytical work is necessary.
Recovery data can play a similar role in evaluating data quality. When matrix spike samples have recoveries that are below the acceptable limits and the uncorrected results are close to regulatory limits, there may be cause for additional analysis before it can be determined that samples are actually below regulatory limits.

6.10 USABILITY OF DATA AS EVIDENTIARY MATERIAL FOR LITIGATION.

What is acceptable as legal evidence is beyond the scope of this manual. A court will usually accept evidence that is generated by methods specified by laws or generally accepted by the scientific community. For this reason laboratory and field procedures should be based on EPA, or other standard-setting organizations. Secondly, and just as important, there must be documentation to support all reported results. The correct procedures may have been used and valid data may have been generated, but they will be of limited value as evidence unless proper documentation such as chain of custody exists.

To assess data on this level, much more information is necessary than that usually contained in a laboratory report. However, this information should be available in the raw data packages for review if needed.

Considering that legal action sometimes occurs years after the fact, it is impossible for a chemist or sampler to recall from memory or even from notes every detail of a sampling or analysis. For this reason, standard operating procedures are used to ensure that operations will be consistent and analytical results will be retrievable.

6.11 DATA INTERPRETATION EXAMPLE.

The following is an example of data interpretation including both field and laboratory work. The original data package is too voluminous to include in this manual but the reader can see that many indicators of data quality are identified and discussed.

CALIFORNIA DEPARTMENT OF TOXIC SUBSTANCES CONTROL
Environmental Chemistry Laboratory

Casmalia Resources, Groundwater
Sampling Dates: 5/19/86 to 5/21/86

DATA EVALUATION

The following discussion focuses on positive laboratory results, by category of analysis. The superscripts (i.e., [a], [b], and [c]) denote the three laboratories conducting the analyses. For more detail, consult the corresponding sections of the field report, QA report, or lab reports.

Purgeable Halocarbons:

Chloroform detected in both replicates of groundwater from A-2B from three analyses give consistent results: 11/54[a], 8.5/73[b], 13/140[c] ug/L. According to Chuck Stultz (DHS/DTSC-LA), there may have been some bailer malfunction during collection of the first sample, leading to loss of volatiles. The second sample may, therefore, be more representative of groundwater at A-2B.

Dichloromethane (Methylene Chloride) was detected in C-1B at 29[a]/24[b]/20[a] ug/L, in A-2M at 23[a]/25[c] ug/L, and in B-2M at 6.3[a]/3[c] ug/L and in a few other wells at close to the detection limit. Dichloromethane is a common lab solvent and often occurs as a random contaminant in samples. Because dichloromethane was detected in both VOA vial samples from the above wells, the results may be representative of the groundwater at these locations.

Tetrahydrofuran (THF) was detected in the sample from C-1B at 450[b] ug/L and in C-6B at 800[b] ug/L. THF was detected but not quantitated by method 624 at SRL. The THF results are consistent with earlier results from EPA and could be due to PVC glue solvent used in well construction.

1,1-Dichloroethane (1,1-DCA) was detected in C-5 at 5.2[c] ug/L, but as a rerun of this sample yielded less than the detection limit (<0.5 ug/L), the evidence is not conclusive for this compound.

Pesticides/PCBs:

No pesticides or PCBs were detected in any of the samples.

Total Organic Halogen (TOX):

The detection limits for TOX were so high that, while no TOX was detected reliably above the detection limit, low or moderate level contamination would not have been detected were it present.

Base/Neutral/Acid:

Phthalates were detected up to 50 ug/L in many of the wells. These are common contaminants, from contact with plastics. They may be present in the groundwater at these levels. No other B/N or A extractables were detected. Other, non- target compounds were tentatively identified, including 3- bromopentane, 4-chlorocyclohexanol, 3-bromocyclohexane, and 2,5- diethyltetrahydrofuran. If feasible, standards of these compounds should be obtained and used for comparison in future groundwater monitoring in order to confirm or refute their presence.

Metals:

Both dissolved Iron and Manganese are elevated in B-5, suggesting incomplete filtering of mineral material; Iron and Manganese are common constituents of soil minerals. As elevated concentrations of these elements occurs independently in other samples, their source is uncertain.

Dissolved copper appears to be elevated in B-3B. Dissolved selenium appears to be elevated in A-2M. Dissolved chromium was reported at 54 ug/L in A-2B. However, since it was neither detected in the duplicate sample nor in the total analysis above 4 ug/L, the value is not reliable.

General Inorganic:

C-1B showed highest pH, carbonate, and hydroxide values while showing low sulfate and

bicarbonate. These results are consistent with the low metals results for the same sample. These results may result from a poor seal between the well screening and the grout, or it could be due to contamination. B-3B showed the highest suspended solids, and nitrate values. The nitrate values exceed drinking water standard, but may be due to either formation or contaminants.

Conductivity is high in B-3M, B-5, and C-5. The latter two are collection (gallery) wells and are expected to catch contamination from the ponds. B-3M may reflect leachate (the only mantel well below B-5).

6.12 REFERENCES.

1) Laboratory Documentation Required for Data Evaluation, Quality Assurance Management Section, USEPA Region IX, R9QA/004.2, August 2001.

2) Principles of Environmental Analysis. American Chemical Society. Anal. Chem. 1983, 55, pp 2210-2218.

   An excellent discussion of environmental measurements including planning, sampling, analysis and reporting. Brief (9 pages) and readable; many valuable references are cited.

3) John Keenan Taylor, Quality Assurance of Chemical Measurements. Lewis Publishers, 1990, pp 7-10.

4) Helsel, Dennis R., Less than Obvious; Statistical Treatment of Data Below the Detection Limit, Environ. Sci. Technol., Vol 24, No. 12., pp 1766-1774, 1990.